Supplementary Information for “Molecular explanation for why talc surfaces can be both hydrophilic and hydrophobic”

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A: Unit cells

The unit cells used for the simulation of talc and pyrophyllite are reported in table 1 and table 2. For fluorotalc, the oxygen of the hydroxyl group is replaced by a fluorine atom and the hydrogen is removed. The unit cell of pyrophyllite, a dioctahedral smectite, has dimensions along the surface of 5.18×8.97 Å^2, as known from X-ray diffraction.[1] The unit cell of fluorotalc is not known exactly; we used the one determined by X-ray diffraction on synthetic fluorohectorite,[2] which differs from fluorotalc only by substitution of some magnesium by lithium in the octahedral layer, resulting in a permanent negative charge compensated by sodium counterions. The unit cell has dimensions 5.24×9.09 Å^2 along the surface. For talc we used the same structure, replacing each fluorine by a hydroxyl group with a bond length of 1 Å, oriented perpendicular to the surface.

B: Comparison of force fields

In the present work, we used the CLAYFF force field to describe the clay surfaces and their interactions with water molecules. To justify this choice, here we compare the predictions of another commonly used force field, and those of CLAYFF, with experimental results. This force field was originally developed by Skipper *et al.*[3] and adapted by Smith *et al.*[4] for its use in conjunction with the SPC/E water model.

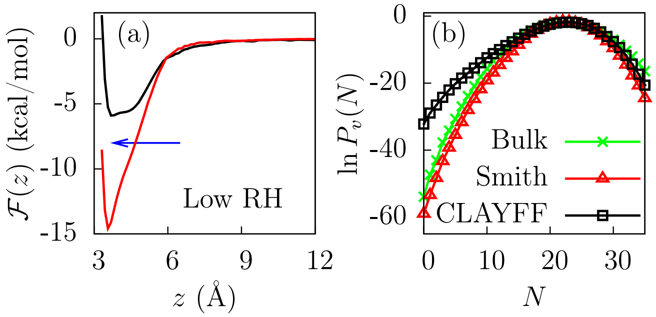

Figure 1: (a) $\mathscr{F}(z)$ for the adsorption of an isolated water molecule on talc simulated using the CLAYFF and Skipper/Smith force fields. The arrow indicates the experimental value of the minimum, estimated by fitting the adsorption isotherm of Michot *et al.*[5] to a Langmuir model in the very low RH regime (see text). (b) $P_{\mathrm{v}}(N)$ for the talc surface, using the CLAYFF and Skipper/Smith force fields.

To investigate the talc surface at low RH, in Figure 1(a), we show the $\mathscr{F}(z)$ obtained using the Skipper/Smith force field and compare it with that obtained using the CLAYFF force field. Also shown is the experimental estimate discussed in the main text, indicating that the Skipper/Smith force field overestimates the binding or adsorption

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free energy.

To investigate the hydrophobicity of talc surfaces at saturation, obtained using the two force fields, in Figure 1(b), we show the respective $P_{\mathrm{v}}(N)$ distributions. $P_{\mathrm{v}}(N)$ for v near the Skipper/Smith talc surface indicates that it is harder to empty the observation volume close to the surface than in bulk water. This is also consistent with the observed complete wetting of the talc surface by a droplet, indicating a contact angle of $\theta = 0^\circ$. Such a complete wetting is however in contradiction with the experimental contact angle of $80-85^\circ$. We thus conclude that the Skipper/Smith force field significantly overestimates talc-water adhesive interactions, both at low RH and at saturation.

Another force field used to model dioctahedral clays and their interaction with organic cations was proposed by Heinz *et al.*[6] This model was not extended to triocahedral clays such as talc, and the behavior of water at clay surfaces modeled with this force field has not been reported. We nevertheless simulated water droplets on the surface of pyrophyllite using this force field. The resulting contact angle (125°) was larger than that measured experimentally ($80-85^\circ$), suggesting that this force fields results in surfaces that are too hydrophobic.

Finally, while we find that CLAYFF is the best available force field to date, to simulate water at the surface of uncharged clay minerals, the present work suggests that it is too hydrophobic. Thus we find that there is room for improvement to describe the clay-water interaction, in agreement with the findings of a recent study comparing molecular simulations with X-ray and neutron diffraction experiments on a charged smectite.[7] The insights gained during the present study of neutral clays, which are more sensitive to the clay-water interactions, could also be helpful in the design of an improved force field. Such design requires a subtle balance between different interactions which is generally not achieved by tuning only one parameter. With this caveat in mind, we note that a slightly more polar hydroxyl group might be relevant, as the modified talc surface with $\delta q = 0.1$ seems to agree quite well with experimentally measured $\Delta\mu_{\mathrm{ads}}$ and $\cos\theta$ values for talc.

C: H-bonds donated by surface OH groups

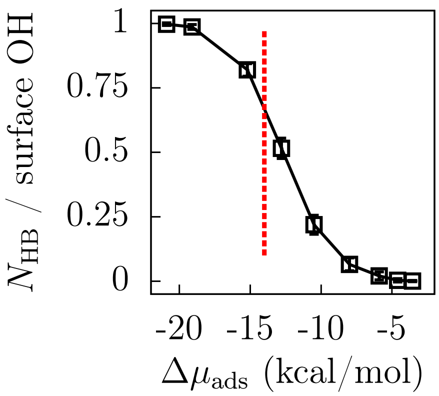

Figure 2: Number of H-bonds donated by the modified talc surface hydroxyl groups to interfacial water molecules as a function of the binding strength $\Delta\mu_{\mathrm{ads}}$.

References

(1) Maegdefrau, E.; Hoffman, U. *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.* **1937**, *98*, 299–323.

(2) Breu, J.; Seidl, W.; Stoll, A. *Z. anorg. allg. Chem.* **2003**, *629*, 503–515.

(3) Skipper, N.; Refson, K.; McConnell, J. *Clay Minerals* **1989**, *24*, 411–425.

(4) Smith, D. *Langmuir* **1998**, *14*, 5959–5967.

(5) Michot, L. J.; Villieras, F.; Francois, M.; Yvon, J.; Le Dred, R.; Cases, J. M. *Langmuir* **1994**, *10*, 3765–3773.

(6) Heinz, H.; Koerner, H.; Anderson, K. L.; Vaia, R. A.; Farmer, B. L. *Chem. Mater.* **2005**, *17*, 5658–5669.

(7) Ferrage, E.; Sakharov, B. A.; Michot, L. J.; Delville, A.; Bauer, A.; Lanson, B.; Grangeon, S.; Frapper, G.; Jiménez-Ruiz, M.; Cuello, G. J. *J. Phys. Chem. C* **2011**, *115*, 1867–1881.

Table 1: Atomic coordinates in the talc unit cell. Subscripts for oxygen differentiate tetrahedral (Td), bridging (B) and octahedral (Oh) atoms.

Atom	X	Y	Z
Mg	1.753	1.514	0.0
	1.753	4.547	0.0
	1.753	7.58	0.0
	4.373	0.0	0.0
	4.373	3.032	0.0
	4.373	6.061	0.0
Si	0.0	1.517	-2.724
	0.0	7.577	-2.724
	2.62	3.029	-2.724
	2.62	6.064	-2.724
	0.887	3.029	2.724
	0.887	6.064	2.724
	3.507	1.517	2.724
	3.507	7.577	2.724
O_B	0.003	7.574	-1.122
	0.003	1.519	-1.122
	2.623	3.027	-1.122
	2.623	6.066	-1.122
	0.884	3.027	1.122
	0.884	6.066	1.122
	3.504	1.519	1.122
	3.504	7.574	1.122
O_{Td}	1.319	2.258	-3.320
	1.319	6.835	-3.320
	2.596	4.547	-3.320
	3.939	2.288	-3.320
	3.939	6.806	-3.320
	5.216	0.0	-3.320
	0.911	4.547	3.320
	2.188	2.258	3.320
	2.188	6.835	3.320
	3.53	0.0	3.320
	4.808	6.806	3.320
	4.808	2.288	3.320
O_{Oh}	0.015	4.547	-0.998
	2.635	0.0	-0.998
	0.872	0.0	0.998
	3.492	4.547	0.998
H	0.015	4.547	-1.998
	2.635	0.0	-1.998
	0.872	0.0	1.998
	3.492	4.547	1.998

Table 2: Atomic coordinates in the pyrophyllite unit cell. Subscripts for oxygen differentiate bridging (B), tetrahedral (Td) and octahedral (Oh) atoms.

Atom	X	Y	Z
Al	1.727	0.0	0.0
	1.727	2.99	0.0
	4.317	4.485	0.0
	4.317	7.475	0.0
Si	0.863	1.495	-2.68
	0.863	4.485	-2.68
	3.453	0.0	-2.68
	3.453	5.98	-2.68
	0.0	2.99	2.68
	0.0	5.98	2.68
	2.59	1.495	2.68
	2.59	7.475	2.68
O_B	0.863	1.495	-1.09
	0.863	4.485	-1.09
	3.453	5.98	-1.09
	3.453	8.97	-1.09
	0.0	2.99	1.09
	0.0	5.98	1.09
	2.59	1.495	1.09
	2.59	7.475	1.09
O_{Td}	0.863	2.99	-3.27
	2.158	0.748	-3.27
	2.158	5.233	-3.27
	3.453	7.475	-3.27
	4.748	0.748	-3.27
	4.748	5.233	-3.27
	0.0	4.485	3.27
	1.295	2.243	3.27
	1.295	6.728	3.27
	2.59	0.0	3.27
	3.885	2.243	3.27
	3.885	6.728	3.27
O_{Oh}	0.863	7.475	-1.09
	3.453	2.99	-1.09
	0.0	0.0	1.09
	2.59	4.485	1.09
H	1.326	6.675	-1.0
	3.916	2.19	-1.0
	2.127	5.285	1.0
	4.717	0.8	1.0